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**EFFECTS OF LOW CHROMIUM(III)
CONCENTRATION IN ELECTRODEPOSITION
OF LOW CONTRACTION CHROMIUM**

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M. D. MILLER

S. K. PAN

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The effects of low chromium (Cr) (III) concentrations on the electrodeposition of low contraction (LC) chromium were studied. A systematic experiment was performed with a Cr(III) concentration range of 0.8 to 10.2 g/l and the following standard LC plating parameters: 250-g/l chromic acid solution, 97-A/dm ² current density, and 85°C bath temperature. On the basis of mechanical properties and the microstructure of the deposits, it was found that lower Cr(III) concentrations yielded higher hardness values, lower (CONT'D ON REVERSE)		

20. ABSTRACT (CONT'D)

tensile strengths, and decreased current efficiencies. The grain size of the deposits also became larger as the Cr(III) concentration decreased.

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INTRODUCTION

The significance of the chromium (Cr)(III) ion to the electrodeposition of chromium is well known (ref 1). Chromium plating solutions containing pure chromic acid and a certain amount of sulfate yield either poor deposits or none at all. A small amount of Cr(III) is needed to deposit chromium. However, too much Cr(III) may have a detrimental effect on the deposit by increasing stress and solution resistance and by reducing chromium adhesion to the substrate (ref 2). The ideal amount of Cr(III) to have in the bath is debatable. Different reports have suggested keeping the Cr(III) concentration below 7.5 g/l (ref 2), below 4.0 g/l (ref 3), or "as little as possible" (ref 4).

A recent report by Pan et al. (ref 5) studied the effects of current density (CD), chromic acid/sulfuric acid ratio, and Cr(III) concentration on low contraction (LC) chromium deposits. This experiment studied Cr(III) concentrations of 4.0, 14.0, 24.0, and 34.0 g/l and their effect on physical properties such as hardness, ultimate tensile strength (UTS), and microstructural growth. However, the analysis of a typical chromium plating bath would most likely reveal a Cr(III) concentration range of between 1 and 10 g/l. Therefore, to truly study the effects of low Cr(III) concentrations on LC chromium deposits, more than one concentration in the 1- to 10-g/l range should be examined. Pan et al. reported that the tensile strength and hardness increased and the current cathode efficiency (CCE) slightly decreased as the Cr(III) concentration decreased. This study analyzes Cr(III) concentrations in the 0.8- to 10.2-g/l range to determine if the trends suggested in the previous report (ref 5) hold up under more realistic Cr(III) concentrations.

EXPERIMENTAL PROCEDURE

The experimental procedure in this report was carried out identically to the one used in Reference 5, with two exceptions. First, this report did not attempt to study the effects of sulfuric acid or CD on the deposit, but focused on the effects of low Cr(III) concentrations. Secondly, solutions with various Cr(III) concentrations had to be prepared for this report. Since the prepared stock solution yielded a Cr(III) concentration of 6.2 g/l, plating solutions of lower Cr(III) concentrations were prepared by taking one-liter amounts of the stock solution and oxidizing the Cr(III) to Cr(VI). This was accomplished by plating "dummy samples" using a lead anode, a cylindrical copper cathode (as mentioned in Reference 5), and a 30:1 anode/cathode ratio. "Dummy samples" plated at 15.1 A/dm² for 24, 48, and 72 hours, whose solutions were then adjusted to 250 g/l chromic acid, yielded solutions whose Cr(III) concentrations were 2.3, 1.1, and 0.8 g/l, respectively.

Plating solutions of higher Cr(III) concentrations were prepared by taking one-liter amounts of the stock solution and reducing the Cr(VI) to Cr(III). As in the previous report (ref 5), this was accomplished by adding the appropriate amounts of oxalic acid to obtain Cr(III) concentrations of 8.2 and 10.2 g/l.

RESULTS AND DISCUSSION

For each of the Cr(III) concentrations studied, five specimens were prepared. The results, averaged from the specimens in terms of CCE, microhardness, and UTS, are summarized in Table I.

Effects of Chromium(III) Concentration

As mentioned in Reference 5, high internal stresses, growth defects in the chromium, and random premature failure of the chromium deposit made the UTS values scatter under a given condition. For this reason, a range of values is

given rather than an average value. This is also the reason why UTS values obtained at 4.0 g/l in the previous report (ref 5) may not exactly match the UTS values at 4.0 g/l in this report.

Figure 1 shows the UTS as a function of low Cr(III) concentration for LC chromium deposits. It is shown that as the Cr(III) concentration increased from 0.8 to 10.2 g/l Cr(III), the UTS initially increased, peaking in the 52- to 58-ksi range at 2.3 g/l Cr(III). The UTS gradually decreased beyond 2.3 g/l Cr(III), reaching a low range of 44 to 48 ksi at 10.2 g/l Cr(III). Any increase in Cr(III) concentration beyond 2.3 g/l appears to have a detrimental effect on the UTS. However, decreasing the Cr(III) concentration below 1.1 g/l Cr(III) also appears to have a detrimental effect on the tensile strength. An optimal range between 1.1 and 2.3 g/l Cr(III) exists. When ideal conditions are not possible, the Cr(III) concentration could be kept in the 0.8- to 6.2-g/l range without a significant decrease in tensile strength. Cr(III) concentrations above 6.2 g/l will result in electrodeposits with significantly lower tensile strengths.

The effects of low Cr(III) concentration on the CCE are shown in Figure 2. The CCE increased slightly, from 11.8 to 12.4 percent, as the Cr(III) concentration increased from 0.8 to 10.2 g/l Cr(III). This rather small increase in CCE is contradictory to many reports (refs 2,4) which say the CCE decreases as the Cr(III) concentration increases (higher solution resistance).

There are two theories why the CCE increased. Kasaaian (ref 6) studied the cathodic film of a chromium plating solution containing Cr(III) ions. He found that the cathodic film contained a significantly higher concentration of Cr(III) ions than the plating solution. A portion of the current must be used to produce enough Cr(III) to compensate for the Cr(III) loss by diffusion and to

maintain a stable cathodic film. As more Cr(III) is added to the plating solution, the diffusion rate is reduced. As a result, less Cr(III) has to be produced and a greater portion of the current goes toward depositing chromium.

The second theory pertains to the findings of Lamb and Young (ref 7). While plating a 0.50-caliber machine gun barrel, they found an increase in CCE and a better axial distribution of chromium as the Cr(III) concentration increased. Knill and Chessin (ref 2) believe that when a long, small diameter anode is used (similar to our study), there is an increase in solution resistance as the Cr(III) concentration is increased. The increasing solution resistance tends to counter the poor current distribution in a long, small cross-sectional area anode. As the solution resistance is increased, the current flows farther along the anode before passing through the solution to the cathode.

The effects of low Cr(III) concentration on hardness are shown in Figure 3. The hardness decreased sharply from 812 KHN to 677 KHN as the Cr(III) concentration increased from 0.8 to 2.3 g/l. As the Cr(III) concentration increased from 2.3 to 10.2 g/l, there was a slight decrease in the hardness. The reason for this trend may be because as the CCE decreases, the amount of hydrogen embrittlement increases, resulting in a more brittle and harder chromium.

Photomicrographs of topographies of LC chromium deposited at various Cr(III) concentrations are shown in Figure 4. The grain size of the chromium deposits became smaller and less pronounced as the Cr(III) concentration decreased. As mentioned previously, the smaller Cr(III) concentration corresponds to higher tensile strengths and increased hardness. Compared to larger grain sizes, smaller grains are less likely to have growth defects and high stress risers, which result during the coalescence of crystallites.

Photomicrographs of the cross-sectional microstructure of LC chromium deposited at various Cr(III) concentrations are shown in Figure 5. The bottom part of the photomicrograph shows the chromium-copper (substrate) interface. A columnar cross-fibrous grain structure is typical of most of the deposits, regardless of the Cr(III) concentrations. There are no major differences in the cross section at any of the Cr(III) concentrations.

CONCLUSIONS

The effects of low Cr(III) concentrations on LC chromium deposits have been investigated. Based on the results of experimental studies, the following conclusions can be drawn:

1. Chromium electrodeposited at 250 g/l, 85°C, and ranging from 0.8 to 10.2 g/l, Cr(III) is crack-free and has a columnar fibrous grain structure, regardless of the Cr(III) concentration.
2. The grain size of the LC chromium deposits becomes larger and more pronounced as the Cr(III) concentration increases.
3. Optimal tensile strengths of 52 to 58 ksi can be obtained when the Cr(III) concentration is kept between 1.1 and 2.3 g/l.
4. The CCE increases slightly (from 11.8 to 12.4 percent) as the Cr(III) concentration increases from 0.8 to 10.2 g/l Cr(III).
5. Maximum hardness can be obtained at lower Cr(III) concentrations. For 1.1 to 2.3 g/l Cr(III), hardness of approximately 675 KHN can be expected.

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TABLE I. EFFECTS OF CHROMIUM(III) CONCENTRATION IN
ELECTRODEPOSITION OF LOW CONTRACTION CHROMIUM

Specimen Group No.	Cr(III) (g/l)	CCE (%)	Hardness (KHN)	UTS (ksi)
CRO3-1	0.8	11.8	812	50-53
CRO3-2	1.1	11.8	699	52-58
CRO3-3	2.3	11.9	677	54-58
CRO3-4	6.2	12.0	673	50-56
CRO3-5	8.2	12.3	674	48-51
CRO3-6	10.2	12.4	656	44-48

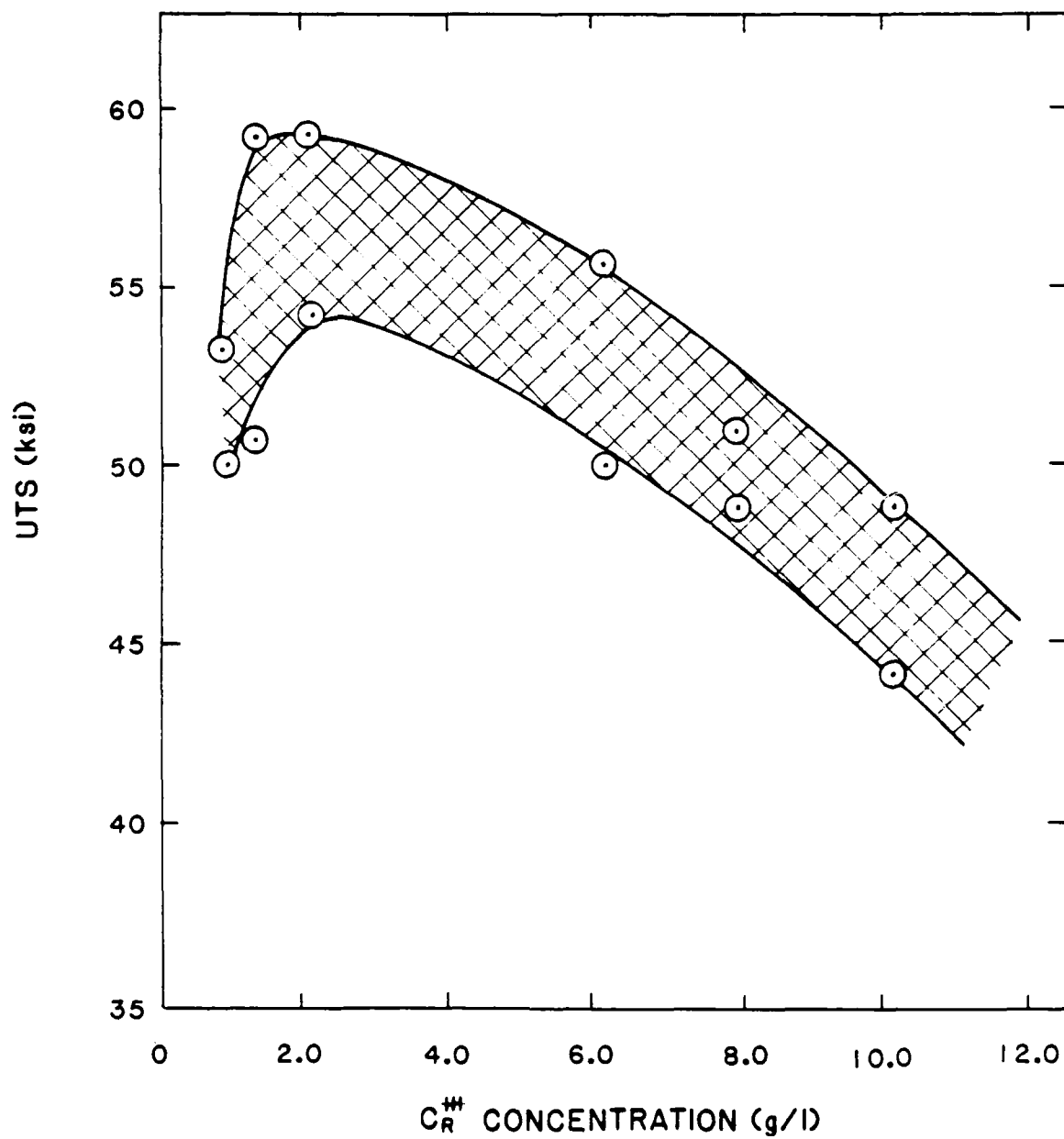


Figure 1. Effects of low chromium(III) concentration on ultimate tensile strength of electrodeposited low contraction chromium.

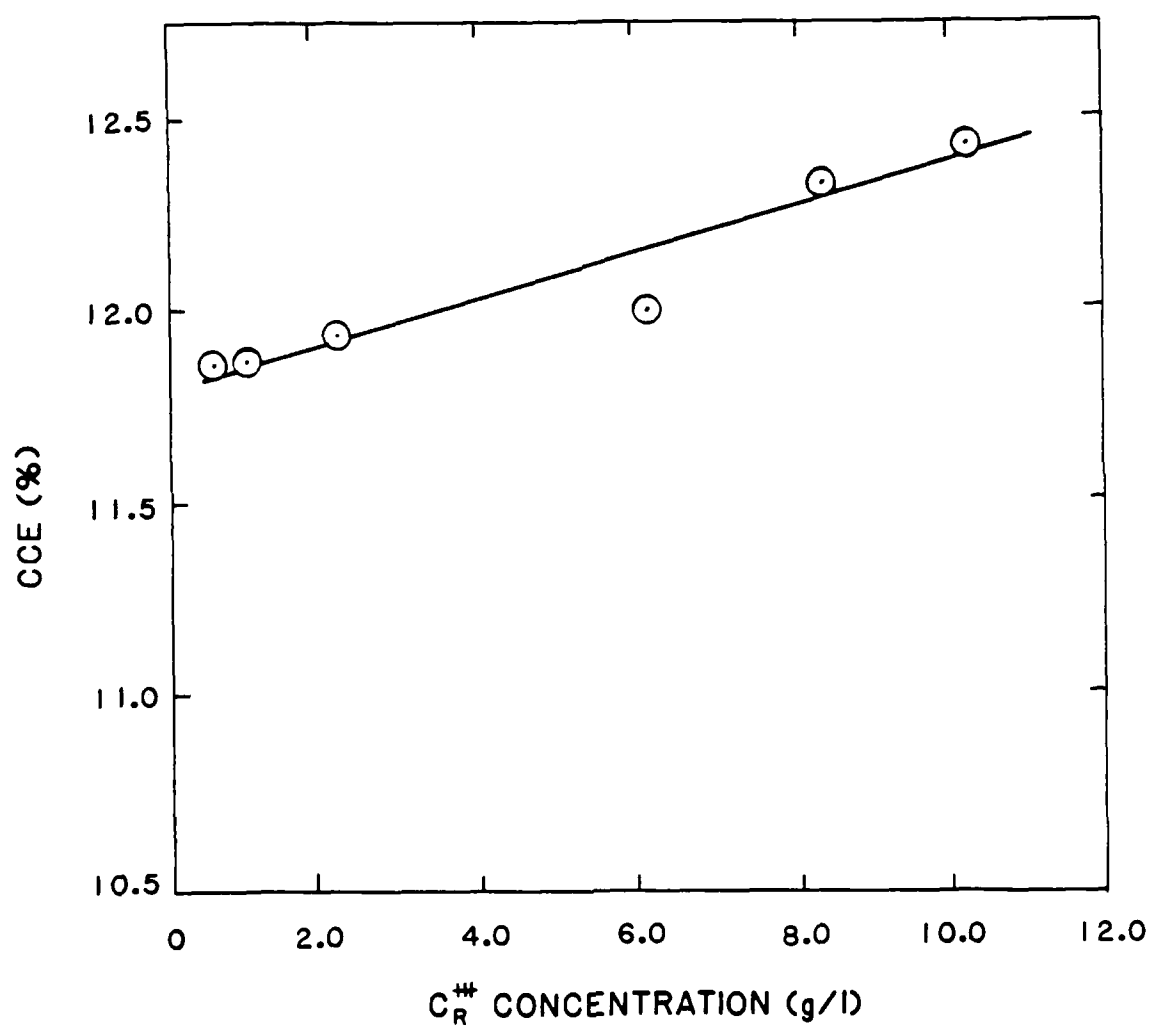


Figure 2. Effects of low chromium(III) concentration on cathode current efficiency of electrodeposited low contraction chromium.

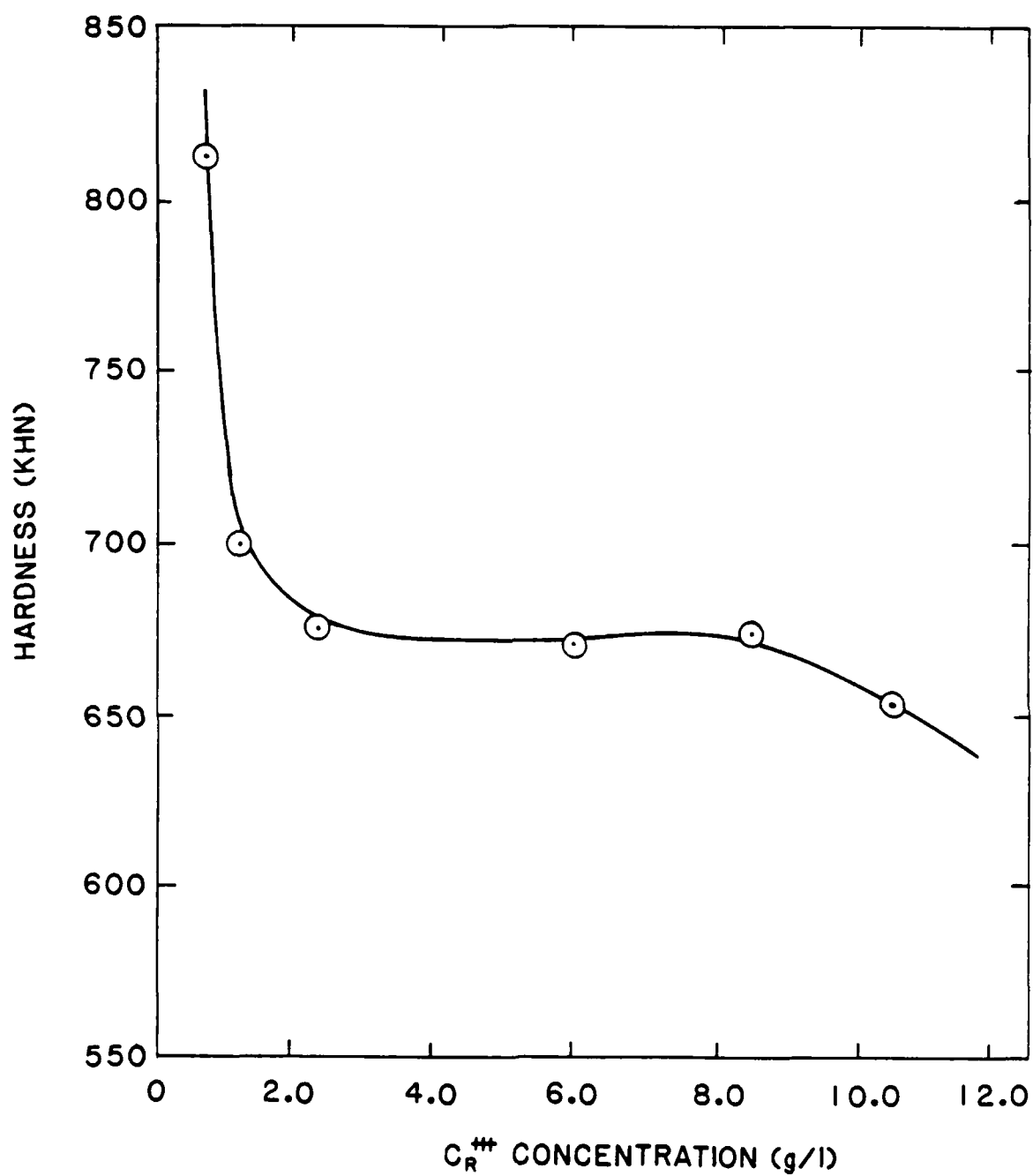


Figure 3. Effects of low chromium(III) concentration on hardness of electrodeposited low contraction chromium.

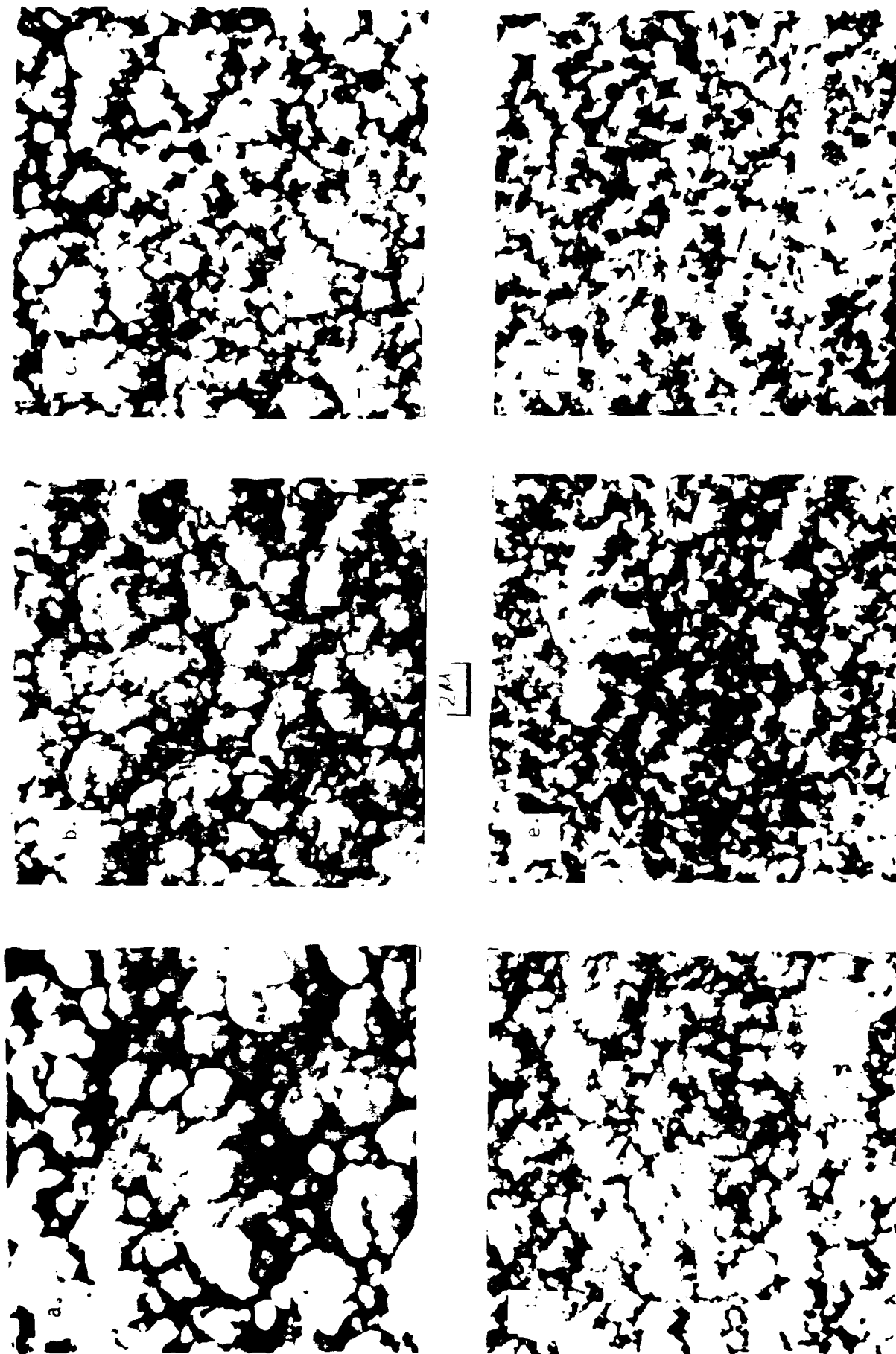


Figure 4. Topographies of low contraction chromium electrodeposited at chromium(III) concentrations of (a) 10.2 g/l, (b) 8.2 g/l, (c) 6.2 g/l, (d) 2.3 g/l, (e) 1.1 g/l, and (f) 0.8 g/l.

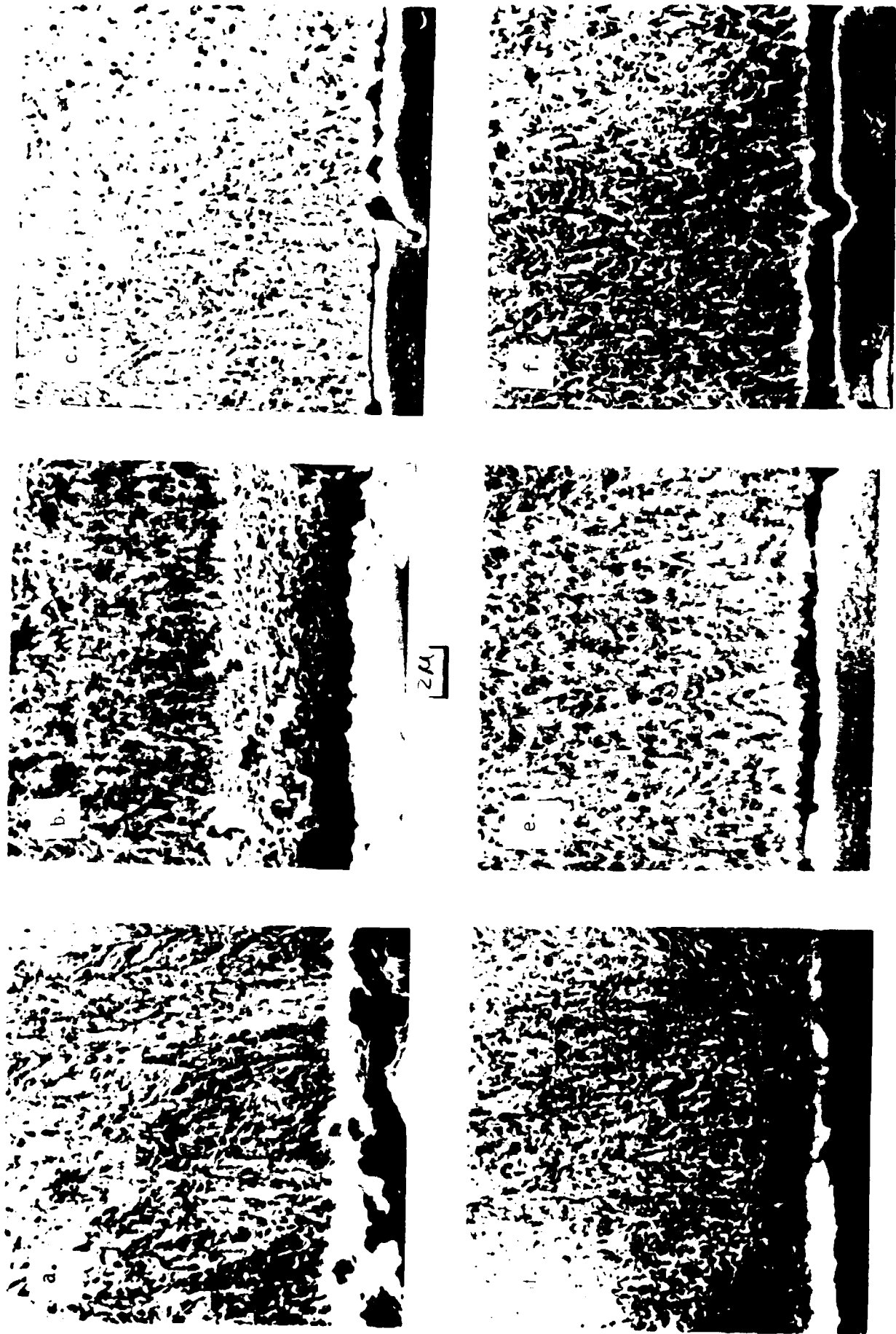


Figure 5. Microstructures of electrodeposited low contraction chromium deposited at chromium(III) concentrations of (a) 10.2 g/l, (b) 8.2 g/l, (c) 6.2 g/l, (d) 2.3 g/l, (e) 1.1 g/l, and (f) 0.8 g/l.

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